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Japanese Kokai Patent Application No. Hei 6[1994]-163481

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JAPANESE PATENT OFFICE  
PATENT JOURNAL  
KOKAI PARENT APPLICATION NO. HEI 6 [1994]-163481

Technical Disclosure Section

Int. Cl.<sup>5</sup>: H 0 1 L 21/302

Sequence Nos. for Office Use: 9277-4M  
A 9277-4M  
F 9277-4M

Application No.: Hei 4 [1992]-333638

Application Date: November 18, 1992

Publication date: June 10, 1994

No. of claims 2 (Total of 7 pages)

Examination Request: Not requested

SEMICONDUCTOR DRY ETCHING METHOD

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[There are no amendments to this patent.]

## Abstract

### Objective

The objective is to present a method for forming a trench on a silicon substrate through control.

### Configuration

A reactive ion etching (RIE) was used as a dry etching device; and HBr as a Br family gas, SF<sub>6</sub> as a halogen family gas, and a N<sub>2</sub> gas were used for the etching gas. As a result, it was possible to set the angle of the side wall to a desired angle ranging from approximately 60° to 90° by means of N<sub>2</sub> flow rate control without lowering SiO<sub>2</sub> selection ratio; besides, it was also possible to reduce the etching residue by SF<sub>6</sub>. Surface of the side walls of the trench were very smooth, and the bottom was kept well-shaped under a fairly wide range of conditions. The etching rate was approximately

800 nm/min, yielding a sufficiently practical production level. A method capable of controlling the angle of the side walls and creating a trench at a high reproducibility rate through the utilization of the etching gas mixture of the present application example while controlling the flow rate to reduce etching residue drastically was presented.

	エッチャングガス	側面角度	SiO <sub>2</sub> 選択比	ボーリング	エッチャング速度	エッチャング回数
①	HBr/SF <sub>6</sub> /N <sub>2</sub>	87°	25	○	800 nm/分	17回/チップ
比較例①	HBr	88°	25	○	750 nm/分	40回/チップ
比較例②	HBr/SF <sub>6</sub>	85°	25	○	800 nm/分	30回/チップ
比較例③	HBr/SiF <sub>4</sub> /HeO <sub>2</sub>	×	52	-	1200 nm/分	100回以上
比較例④	HBr/Cl <sub>2</sub> /HeO <sub>2</sub>	81°	21	○	350 nm/分	20回/チップ

Key: 1 Present application example  
 2 comparative example  
 3 Etching gas  
 4 Side wall angle  
 5 SiO<sub>2</sub> selection ratio  
 6 Bowing  
 7 Etching rate  
 8 Etching residue  
 9 No  
 10 Yes  
 11 Min  
 12 Unit  
 13 Or more

### Claims

1. Dry etching method for etching a silicon substrate, characterized in that a mixed gas comprising a gas containing bromine, a gas containing a halogen element, and a nitrogen gas is used; and the etching rate and the angle of the trench are controlled by setting the flow rate of the aforementioned nitrogen gas to a prescribed ratio relative to the flow rate of the aforementioned bromine-containing gas.

2. Dry etching method described under Claim 1 characterized in that, the nitrogen gas content is 1-50% or less relative to that of the bromine-containing gas.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to a method for shaping a trench and a pit by means of dry etching on a substrate, which is useful in the area where Si is used as a material to produce products, particularly, DRAM semiconductor devices.

[0002]

Prior art

The deep recess (trench) created by selectively etching deep into the surface, the object the present invention intends to achieve, is needed to realize high level of integration and voltage resistance of semiconductors. From the viewpoint of semiconductor production process and semiconductor characteristics, as shown in Figure 1 (a), it is preferable that the sides taper slightly and smoothly, and the bottom forms a semicircle in terms of the shape, necessitating the establishment of the shaping technology for this. Undesirable shapes are those shown in Figures 1 (b) through (h).

[0003]

Conventionally, dry etching on Si is not limited to a trench (the same for a pit, but only trenches will be mentioned hereinafter); wherein, as disclosed in Japanese Kokoku Patent No. Sho 57 [1982]-11954 and Japanese Kokoku Patent No. Sho 59 [1984]-22374, a gas containing fluorine (will be designated as "F family gas" hereinafter), a gas containing chlorine (will be designated as "Cl family gas" hereinafter), and a gas containing bromine (will be designated as "Br family gas" hereinafter) are being used widely. In general, as shown in Figure 2, after an insulating  $\text{SiO}_2$  mask (202) is formed on an Si substrate (201) (Figure 2 (a)), a pattern is created on the mask (Figure 2 (b)), and etching is applied (Figure 2 (c)) to form a trench. Here, processes, such as integrated circuit formation, are omitted.

[0004]

At the present time, while attempts are being made to realize the formation of a trench using an RIE (Reactive Ion Etching) device and applying an etching gas atmosphere made of a Br family gas, an F family gas, and a Cl family gas, for example, no method reliable enough to be used for production is yet known. Some known methods report that the shape of the side walls of a trench can be controlled when an  $\text{SiCl}_4$  etching gas and an inert gas are mixed, and dry etching is applied while the gas pressure is controlled.

[0005]

Problem to be solved by the invention

Incidentally, when forming the trench in Figure 2 (c), not only the Si substrate (201) part but also a part of the SiO<sub>2</sub> mask (202) are made thinner by the etching during said process. The indication of the unlikeliness of the reduction of said mask is the "SiO<sub>2</sub> selection ratio" wherein, the greater the value is, the more easily the trench is created. When the value of the SiO<sub>2</sub> selection ratio is small, the mask will be gone before a prescribed depth is achieved by etching, and the Si on the substrate ends up being eroded away. Therefore, there is a problem that while an etching gas with greater SiO<sub>2</sub> selection ratio is in demand, F family gases usually have a low SiO<sub>2</sub> selection ratio, and isotropic etching, by which the reaction proceeds in all directions, is likely to occur.

[0006]

In addition, as semiconductor devices gain diversity and higher performance, the etching residue needs to be reduced during the formation of the trench in order to improve the yield. As shown in Figure 4, mechanism of the formation of etching residue can be explained as the adherence of dust and particles (404) onto the parts (403) where the Si is exposed on the mask under the condition of (a) prior to etching, or pieces of the mask and the products of the reaction (substances difficult to etch) formed at the time of etching are adhered during the etching, so that normal etching is hindered and ultimately the

conditions (405) shown in Figure 4 (b) are created. This is referred to as black Si or Si black, which creates a problem of deterioration in yield. In general, there is a problem that the amount of black Si increases in the order of F family gases, Cl family gases, and Br family gases. However, there is an advantage that the further forward in the aforementioned order, the better the shape of the side walls becomes.

[0007]

On the other hand, as disclosed in Japanese Kokoku Patent No. Sho 59 [1984]-67635, a general method in which the Si is etched vertically is presented in the prior art. However, depth of the trench was 5  $\mu\text{m}$  or so at most with this method, and when an attempt was made to etch any deeper than that, the shape of the trench lost uniformity. On the contrary, when the shape was to be perfected, the problem of residue occurred. Thus, [said method] had not necessarily reached the level at which trenches having a uniform shape at a highly accurate satisfactory level could be formed. Accordingly, there are cases in which various kinds of etching gases are mixed in order to make best use of their characteristics. However, no etching method which would solve all of the problems and lead to production has yet been suggested.

[0008]

In addition, although U.S. Patent No. 4784720 discloses that products are adhered selectively onto the side walls of a trench in order to control the shape of the trench, a method in which

the shape is controlled through selective adhesion of the aforementioned etching residues is likely to generate etching residues. Leaving the residues alone would lead to the problem of deteriorated yield due to leakage and insufficient voltage breakdown resistance. Thus, processes need to be added to remove [the residues]. In addition, in the aforementioned report providing that  $\text{SiCl}_4$  and an inert gas are mixed and the gas pressure can be used to control the shape of the side walls of the trench, there is no specification of the inert gas, nor is there any mention of other etching gases.

[0009]

The purpose of the present invention is to achieve efficient and highly accurate formation of a reproducible well-shaped trench while solving the aforementioned problem at the same time.

[0010]

Means to solve the problem

In order to solve the aforementioned problem, a silicon substrate etching gas is prepared by mixing a gas containing bromine (designated as "Br family gas" hereinafter), a gas containing halogen elements (designated as "X family gas" hereinafter), and a gas containing nitrogen (designated as " $\text{N}_2$  family gas" hereinafter), and dry etching is carried out. In such case, the flow rate of the  $\text{N}_2$  gas is adjusted according to the intended trench shape.

[0011]

#### Function

When etching is performed with various kinds of parameters, which will be clarified later in an application example, set to appropriate values using the etching gas having the aforementioned composition, etching on the Si substrate is advanced primarily by the Br family gas; the X family gas plays the role of removing the etching residues by means of volatilization; and the N<sub>2</sub> gas controls the Br family gas and the X family gas to prevent over-reaching, which in turn plays the role of controlling the shape in order to achieve the intended trench.

[0012]

#### Effect of the invention

As it will be clarified in the application example later, the angle of the side walls of the trench was controlled by controlling the flow rate of the N<sub>2</sub> gas without deteriorating the SiO<sub>2</sub> selection ratio. In addition, apart from what was just said, residues were reduced drastically by the X family gas. As a result, the intended trench formation method was able to be presented.

[0013]

#### Application example

*mu Marfod*

The present invention will be explained based on a specific application example. The RIE (Reactive Ion Etching) device shown in schematic cross section in Figure 3 was used as the dry etching device. In Figure 3, an etching chamber (301) is provided with an upper electrode (304) and a lower electrode (305), a target Si substrate (308) is placed on said lower electrode (305), an etching gas to be described below is introduced through a gas inlet (302) and discharged from an exhaust opening (303). A 13.56 MHz power is supplied between said electrodes from a high-frequency power source (306) in order to generate gas plasmas for etching the Si substrate. Furthermore, said RIE device is of the magnetron type, wherein a magnetic coil (307) is provided around the etching chamber.

[0014]

The etching gases used with the aforementioned RIE device in the present application example are HBr as the Br family gas, SF<sub>6</sub> as the X family gas, and N<sub>2</sub> gas.

[0015]

Etching was applied to the Si substrate using the aforementioned gas composition with the SF<sub>6</sub> flow rate set to 2 and 3 (SCC), the high-frequency power of the RIE device to 500 (W), pressure of the mixed gas to 100 (mtorr), and magnetic

intensity of the coil indicated by 307 in Figure 3 to 55 (Gauss) while changing the flow rate of the N<sub>2</sub> gas; and the angles (102) of the side walls of the trench were then measured. As a result, a proportional relationship was found to be present in the area where the wall is perpendicular as shown in Figure 5, indicating that the side wall angle can be set to a desired angle between approximately 60 degrees and 90 degrees by adjusting the flow rate of the N<sub>2</sub> gas. Furthermore, as shown in Figure 6, the SiO<sub>2</sub> selection ratio also changes according to the flow rate of the N<sub>2</sub> gas, and it increases as the flow rate increases to the advantage of the formation of the trench.

[0016]

[The mechanism of] said function of the N<sub>2</sub> gas can be inferred as follows. N<sub>2</sub> is broken up by the plasma into N radicals during the etching, and these [radicals] react with Si or etching product in the chemical vapor to create SiN. This [SiN] covers the side walls, which prevents etching from advancing excessively and helps control the angle of the side walls at the same time. Because it also covers the SiO<sub>2</sub> mask at the same time, SiO<sub>2</sub> is prevented from being etched, and the SiO<sub>2</sub> selection ratio is increased as a result.

[0017]

In addition, it has been also confirmed that the surfaces of the side walls become extremely smooth when the N<sub>2</sub> gas is mixed, indicating that it is an effective way to improve the reliability.

[0018]

As shown in Figure 7, it was evident that the etching residues decreased as the SF<sub>6</sub> flow rate increased and disappeared with a relatively small SF<sub>6</sub> flow rate. The amount of etching residue was obtained by comparing the number of residual [particles] per 1-cm-square chip with 10  $\mu\text{m}$  pattern width. As shown in Figure 8, said mechanism can be explained as follows: even if a small object (803) which did not get etched was present on an Si substrate (801), SF<sub>6</sub> is broken up into active F radicals (804) in the plasma, and [these] react with the small object (803) and volatilize (805) it. However, it was found that with the flow rate which eliminates the residues completely, the SiO<sub>2</sub> selection ratio becomes relatively small, that is, approximately 10. This is a disadvantage when creating a deeper trench, but adjustments can be made to optimize it depending on the extension of the trench to be created.

[0019]

With respect to the shape of the trench, it is preferable that the bottom takes an arc (bottom round) shape for the sake of the relaxation of the field and the stress at the bottom part. A variety of tests were conducted regarding said shape. As a result, it was confirmed that desirable bottom shape was maintained under a fairly wide range of conditions, as shown in Figure 9. It was confirmed that N<sub>2</sub> gas demonstrated its effect also when the low rate was within the range of 0-30 (SCCM). In addition, the etching rate, that is, approximately 800 nm/min.

(Figure 12), was confirmed to meet the level for practical production sufficiently.

[0020]

When the etching gas was replaced by another gas in order to compare the amounts of etching residues, the results shown in Figure 10 were obtained. It was clear that the configuration of the present application example as described above was most suitable for trench formation. Figure 11 shows the etching conditions in the application example and the comparative examples.

[0021]

Based on a general view over the aforementioned findings, as shown in Figure 2, it was possible to present a method capable of controlling the side wall angle while reducing etching residues drastically by controlling the flow rate of the etching gas having the configuration of the present application example in order to create a trench at a high reproducibility rate.

[0022]

Furthermore, the X family gas need not be SF<sub>6</sub>, and other gases, such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, CHF<sub>3</sub>, NF<sub>3</sub>, among others, may be used. In addition, the same effect can be achieved by means of an ECR (Electron Cyclotron Resonance) device instead of the RIE device.

### Brief description of the figures

Figure 1 shows cross sections showing various trench shapes, of which (a) is a cross section showing an ideal shape, and (b) through (h) are cross sections showing undesirable shapes.

Figure 2 is a diagram showing simplified trench formation process.

Figure 3 is a cross section showing the schematic configuration of the magnetron RIE (Reactive Ion Etching) device used in the application example of the present invention.

Figure 4 are diagrams showing the mechanism of the generation of etching residues schematically.

Figure 5 is a diagram showing the  $N_2$  flow rate dependency characteristic of the trench side wall angle of the sample used in the application example.

Figure 6 is a diagram showing the  $N_2$  flow rate dependency characteristic of the  $SiO_2$  selection ratio of the sample used in the application example.

Figure 7 is a diagram showing the  $SF_6$  flow rate dependency characteristic of the etching residues.

Figure 8 is a diagram showing the mechanism of the reduction of etching residues by  $SF_6$  schematically.

Figure 9 is a diagram showing the range of setting for the formation of well-shaped trench used in the application example.

Figure 10 is a diagram showing the result of the comparison of the amounts of etching residues between the application example and other etching gases.

Figure 11 is a diagram showing the etching conditions of the application example and the comparative examples.

Figure 12 is a diagram showing the results of the comparison with the etching gases other than those of the application example.

Explanation of reference numerals

- 101. Si substrate
- 102. Trench side wall angle
- 201. Si substrate
- 202. SiO<sub>2</sub> mask
- 203. SiO<sub>2</sub> mask thinned by etching
- 301. Etching chamber of the RIE device
- 308. Si substrate to be etched
- 401. Si substrate
- 402. SiO<sub>2</sub> mask
- 403. Window on the mask pattern (part to be etched)
- 404. Residue (deposit)
- 405. Etching residue (black Si)
- 801. Si substrate
- 802. SiO<sub>2</sub> mask
- 803. Small object, such as dust, which does not get etched
- 804. Fluoride radical
- 805. Volatile substance

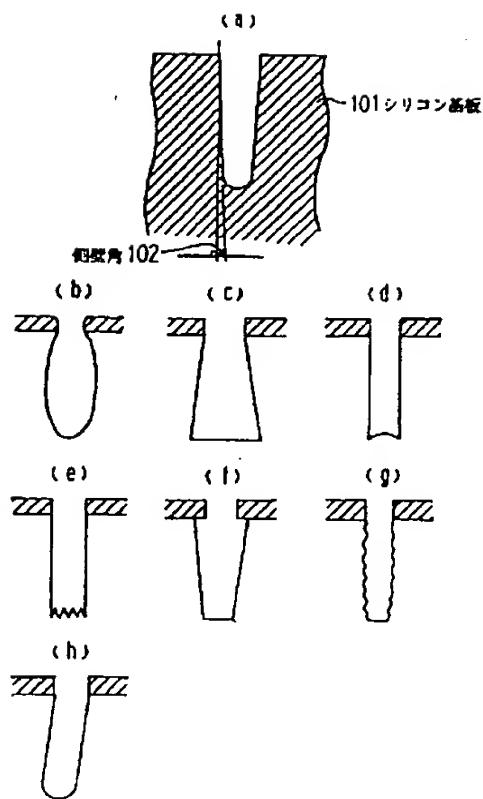


Figure 1

Key: 101 Silicon substrate  
102 Side wall angle

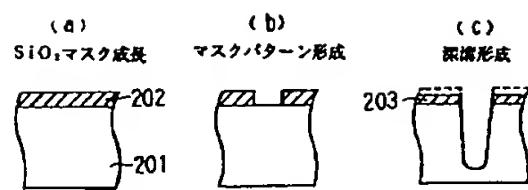


Figure 2

Key:  
a SiO<sub>2</sub> mask growth  
b Mask pattern formation  
c Trench formation

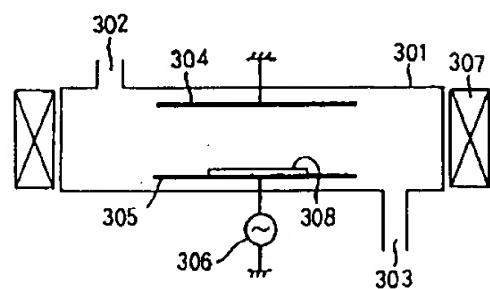


Figure 3

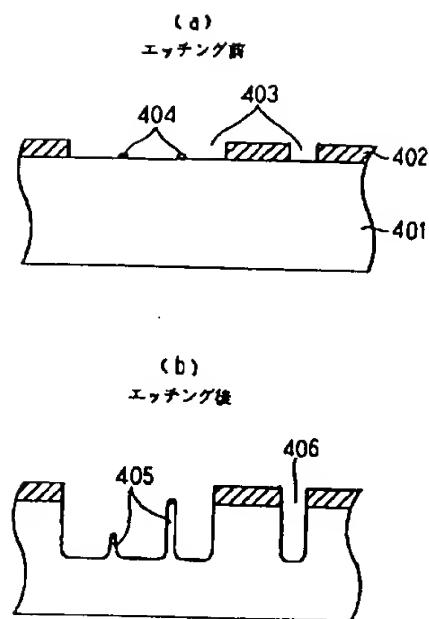


Figure 4

Key: a Before etching  
b After etching

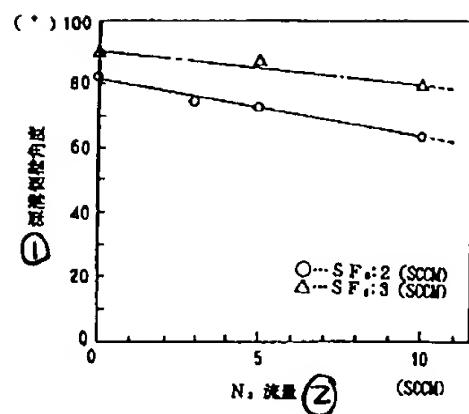


Figure 5

Key: 1 Trench side wall angle  
2  $N_2$  flow rate

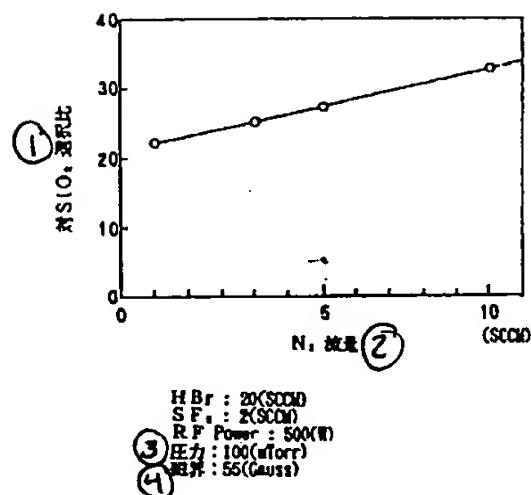


Figure 6

Key: 1  $\text{SiO}_2$  selection ratio  
 2  $N_2$  flow rate  
 3 Pressure  
 4 Magnetic field

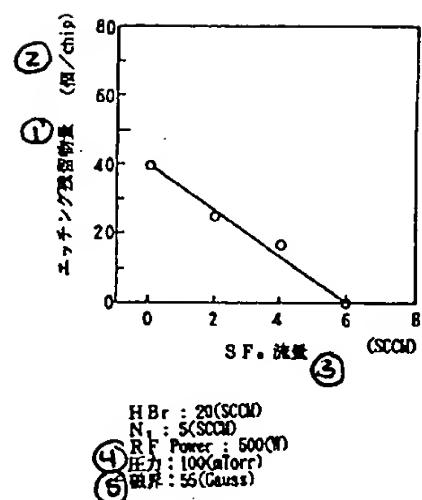


Figure 7

Key:

- 1 Amount of etching residues
- 2 Unit(s)
- 3 SF<sub>6</sub> flow rate
- 4 Pressure
- 5 Magnetic field

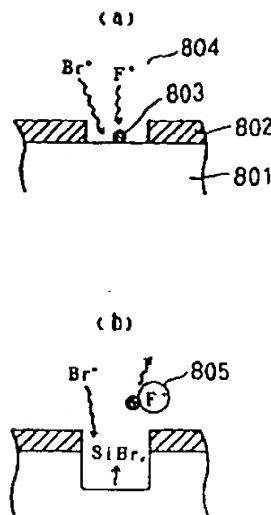


Figure 8

要因①	設定値②
HBr 流量 (SCCM)	10 ~ 100
SF <sub>6</sub> 流量 (SCCM)	2 ~ 10
N <sub>2</sub> 流量 (SCCM)	3 ~ 10
高周波電力 (W) ③	200 ~ 600
ガス圧 ④ (mTorr)	50 ~ 150
磁界強度 ⑤ (Gauss)	0 ~ 100

Figure 9

Key: 1 Factor  
 2 Flow rate  
 3 High-frequency power  
 4 Gas pressure

5 Intensity of magnetic field  
 6 Value to be set

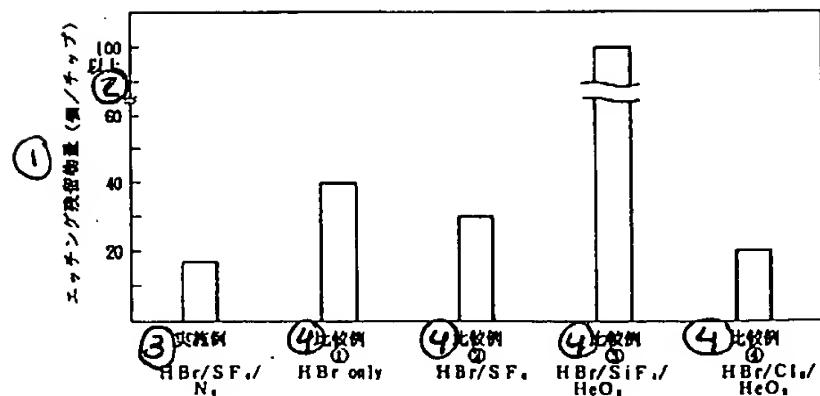


Figure 10

Key: 1 Amount of etching residues  
 2 Or more  
 3 Application example  
 4 Comparative Example

① 実施例及び比較例	実施例	比較例①	比較例②	比較例③	比較例④
	HBr/SF <sub>6</sub> /N <sub>2</sub>	HBr only	HBr/SF <sub>6</sub>	HBr/SiF <sub>4</sub> /HeO <sub>2</sub>	HBr/Cl <sub>2</sub> /HeO <sub>2</sub>
② HBr 流量 (SCCM)	20	80	20	22	30
SiF <sub>4</sub> 流量 (SCCM)	-	-	-	5	-
HeO <sub>2</sub> 流量 (SCCM)	-	-	-	10	4
③ N <sub>2</sub> 流量 (SCCM)	5	-	-	-	-
SF <sub>6</sub> 流量 (SCCM)	3	-	2	-	-
Cl <sub>2</sub> 流量 (SCCM)	-	-	-	-	10
RF Power (W)	500	400	400	420	150
④ 壓力 (mTorr)	100	100	100	100	20
磁界強度 (Gauss)	55	55	55	55	75

Figure 11

Key:

- 1 Application example and comparative example
- 2 Flow rate
- 3 Pressure
- 4 Intensity of magnetic field
- 5 Application example
- 6 Comparative Example

	エッチングガス ③	側壁角度 ④	対 $\text{SiO}_2$ 選択比	ボーリング ⑤ Bowing ⑥	エッチング速度 ⑦	エッチング残留物 ⑧
① 当実施例	$\text{HBr}/\text{SF}_6/\text{N}_2$	$87^\circ$	25	⑨ 無 $\text{no}$	800 nm/分	17個/Chip ⑫
比較例①	$\text{HBr}$	$88^\circ$	25	⑨ 無 $\text{no}$	750 nm/分	40個/Chip ⑫
比較例②	$\text{HBr}/\text{SF}_6$	$88^\circ$	25	⑨ 無 $\text{no}$	800 nm/分	30個/Chip ⑫
比較例③	$\text{HBr}/\text{SiF}_4/\text{He}, \text{O}_2$	$\times$	52	-	1200 nm/分	100 以上 ⑬
比較例④	$\text{HBr}/\text{Cl}_2/\text{He}, \text{O}_2$	$91^\circ$	21	⑩ 有 $\text{yes}$	350 nm/分	20個/Chip ⑫

Figure 12

Key:

- 1 Present application example
- 2 comparative example
- 3 Etching gas
- 4 Side wall angle
- 5  $\text{SiO}_2$  selection ratio
- 6 Bowing
- 7 Etching rate
- 8 Etching residue
- 9 No
- 10 Yes
- 11 Min
- 12 Unit
- 13 Or more